Journal of Hazardous Materials 159 (2008) 435–439

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Coprecipitation of Ni^{2+}, Cd^{2+} and Pb^{2+} for preconcentration in environmental samples prior to flame atomic absorption spectrometric determinations

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ARTICLE INFO

Article history:
Received 30 December 2007
Received in revised form 13 February 2008
Accepted 13 February 2008
Available online 17 February 2008

Keywords:
Coprecipitation
Copper hydroxide
Enrichment
Flame atomic absorption spectrometry

ABSTRACT

A coprecipitation procedure has been presented prior to flame atomic absorption spectrometric determination of nickel, cadmium and lead ions in environmental samples. Analyte ions were coprecipitated by using copper hydroxide precipitate. The influences of some analytical parameters like amounts of copper, sample volume, etc., on the recoveries of the analytes were investigated. The interference of other ions was negligible. Under the optimized conditions, the detection limits (3 sigma, $n = 15$) of lead(II), nickel(II) and cadmium(II) were 7.0, 3.0 and 2.0 μg/L, respectively. The proposed method has been successfully applied for the determination of traces of Ni, Cd and Pb in environmental samples like tap water.

1. Introduction

Heavy metals are major pollutants in marine, lake and ground waters as well as in industrial and even treated effluents. Heavy metals are also major hazards to the soil–plant system [1–4]. They play negative roles in human life. For example, lead is a widely deposited environmental toxicant for neurological, renal, hepatic, and immune systems [5,6]. Nickel is widely used in modern industry. Its overexposure in human beings can provoke significant effects including lung, cardiovascular and kidney diseases [7–9]. The determinations of the heavy metals in environmental samples are important for human health. Flame atomic absorption spectrometry (FAAS) is one of the instrumental techniques for the determination of heavy metal ions at trace levels [10–13]. However, the direct determination of heavy metal ions by FAAS at trace levels in real samples remains a challenging problem because of their low concentration and matrix effects. Lower element concentrations then the quantitation limits of FAAS are another problem in flame atomic absorption spectrometric determinations [14–16]. In order to overcome these limitations, separation–preconcentration methods are used by the analytical chemists [17–19]. Several methods extensively used for preconcentration include liquid–liquid extraction, ion exchange, cloud point extraction, membrane filtration, solid phase extraction and coprecipitation [20–25].

The coprecipitation technique for heavy metal ions is also widely applied for isolation and preconcentration of analytes from a liquid matrix and/or purified extracts. It has some advantages: simple, rapid and analytes could be preconcentrated and separated from the matrix simultaneously. Inorganic and organic coprecipitants have been used successfully in the coprecipitation of heavy metal ions at trace levels.

In the presented work, hydroxide was selected as an inorganic precipitant and copper(II) was selected as a carrier element. According to our literature survey, this combination was not used for the coprecipitation of metal ions. The analytical parameters including pH, amounts of copper, sample volume, etc., on the recoveries of nickel(II), cadmium(II) and lead(II) ions were investigated.

2. Experimental

2.1. Reagents

All the reagents used were of analytical grade. Deionized double distilled water was used throughout the experimental work. Laboratory glassware was kept overnight in a 10% v/v HNO_3 solution and then rinsed with deionized double distilled water. A solution of copper(II) (0.1%) was prepared by dissolving 0.1 g of $Cu(NO_3)_2$ (E-Merck, Germany) in deionized doubly distilled water in 100 mL standard flask. It was prepared daily. Diluted NaOH solutions (0.1 M) were used at the pH adjustments.

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doi:10.1016/j.jhazmat.2008.02.034

Stock standard solutions of analytes, 1000 mg/L, were prepared by dissolving appropriate amount of nitrate salts of analytes in 1% nitric acid. Stock metal ion solutions were diluted daily for obtaining reference and working solutions. The calibration curve was established using the standard solutions prepared in 1 mol/L HNO_3 by dilution from stock solutions.

2.2. Instruments

A Varian AA240 model flame atomic absorption spectrometer was used for determination of analytes. The operating parameters of instruments for nickel, cadmium and lead were set according to the manufacturer recommendation. For measuring pH values in the aqueous phase, WTW 330i model glass-electrode was employed. Ohaus EP214C model analytical balance was used for all mass measurements.

2.3. Model studies

1.0 mL of 0.1% (1 mg) copper(II) was added to 10 mL of solution containing 5–20 μg analyte ions. Then the pH of the solution was adjusted to related pH by the addition of 0.1 mol/L NaOH. After 10 min, the solution was centrifuged at 3500 rpm for 10 min. The supernatant was removed. The precipitate remained adhering to the tube was dissolved with 0.5 mL of concentrated HNO_3. The volume was completed to 5.0 mL by the addition of distilled water. The number of replicates for the test workings was three. The levels of analyte ions were determined by flame atomic absorption spectrometry.

2.4. Applications

0.1 g of salt sample was dissolved in 20 mL of distilled water. Then 1.0 mL of 0.1% copper(II) was added. In order to form a copper hydroxide precipitates, the pH of the solution was adjusted pH 9 by the addition 0.1 mol/L NaOH. The tube is slowly and carefully shaked for several seconds and allowed to stand for 10 min. The precipitate is centrifuged at 3500 rpm for 10 min and the supernatant is discarded. A small precipitate adheres to the bottom of the tube. Then, 0.5 mL of concentrated HNO_3 is added to dissolve the precipitate. The final volume was completed to 2.0–5.0 mL with distilled water. The analyte ions in this solution are determined with flame AAS.

For the analysis of water sample, 0.1% copper(II) was added to 200 mL of water sample analyzed. The pH of the solution was adjusted pH 9 by the addition 0.1 mol/L NaOH to obtain copper(II) hydroxide precipitates. Then the coprecipitation procedure given above was performed.

3. Results and discussion

3.1. Influences of pH

On the coprecipitation works, pH of the working solutions is one of the main factors to obtain quantitative recoveries of the analytes [26–30]. The influences of pH on the recoveries of cadmium, nickel and lead ions were investigated in the pH range of 8–12. pH of the model solutions was adjusted by the addition of 0.1 mol/L NaOH. The results are depicted in Fig. 1. Analyte ions were quantitatively recovered in the pH range of 9–12 except lead(II). Lead(II) was quantitatively recovered in the pH range of 9–11. All subsequent works were performed at pH 9.

3.2. Influences of amounts of copper(II) as carrier element

The influences of amounts of copper(II) as carrier element on the recoveries of analyte ions were also examined by using model solutions at pH 9. The results are given in Fig. 2. The recoveries of analyte ions were not quantitative without copper. Quantitative recoveries were obtained for cadmium(II), nickel(II) and lead(II) ions at the copper amounts range of 0.25–2.0 mg (Fig. 2). All further works were carried out by the addition of 0.1 mg of copper(II) as carrier element.

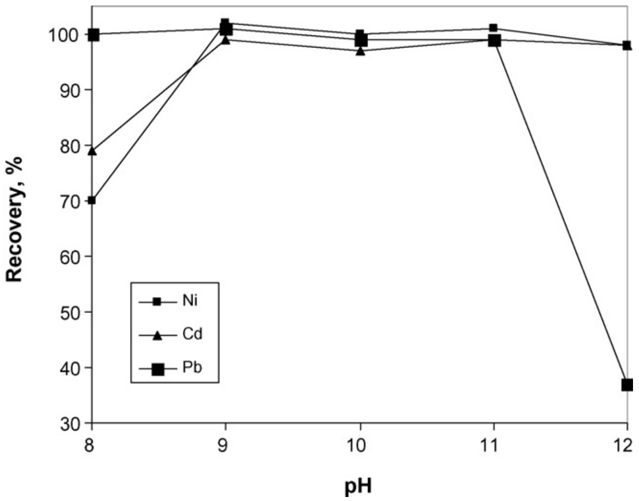

Fig. 1. Effects of pH on the coprecipitation efficiencies of analyte ions (N = 3).

3.3. Effects of duration time for coprecipitation

The influences of duration time for the coprecipitation on the recoveries of analytes were also studies in the time range of 1–20 min. Quantitative recoveries for all the analytes were obtained all the ranges. The studies were performed at 10 min of duration time.

3.4. Influences of centrifugation time

The influences of centrifugation time on the recoveries of analyte ions were investigated at 3500 rpm. Quantitative recoveries for Cd(II), Pb(II) and Ni(II) ions were obtained in the range of 5–25 min. All further works were carried out at 15 min of centrifugation time.

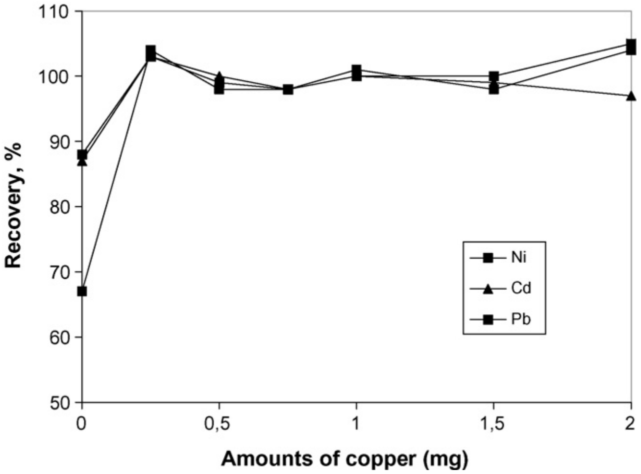

Fig. 2. Influences of copper(II) on the recoveries of analytes (N = 3).